CHIRALITY RECOGNITION IN THE TERNARY AGGREGATES OF PROPYLENE OXIDE: EXPERIMENTALLY GUIDED THEORETICAL CONFORMATIONAL SEARCHES

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Propylene oxide (PO), a simple chiral cyclic ether, has served as a valuable prototype molecule for the theoretical development of chiroptical activities and for rotational spectroscopic studies of chirality recognition . Although a rotational spectroscopic study of the PO dimer was completed more than ten years ago where six homo- and heterochiral structures were identified experimentally3, no similar studies of larger chiral aggregates such as a PO trimer have been reported so far. This is in part because the conformational ensemble space grows exponentially as the size of aggregates increases, making it highly challenging to detect and assign the related rotational spectra. Aided with the recent development in chirped pulse Fourier transform microwave techniques and in meta-dynamics conformational search algorithms , we have explored the conformational space of the PO trimer. Several hundred possible PO trimer structures were predicted the first two most stable homochiral trimers were assigned. The number of possible conformers of the heterochiral PO trimer predicted is about three times of that of the homochiral trimer. Even so, no match could be made for the heterochiral trimer conformers detected, despite additional exhausted conformational searches. By studying all monosubstituted 13C isotopologues of the most stable homochiral and heterochiral PO trimer in nature abundance, we experimentally determined their C atom backbone structures. Guided with this information, additional PO trimer structures were calculated which match the observed rotational constants and dipole moments. The study showcases the power current rotational spectroscopic experiments and highlights the necessity of intensive interplay between experiment and theory in dealing with large aggregates (or molecules). Interesting results on chirality recognition in the PO trimer will also be discussed.

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